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NMR AND ESR CHARACTERIZATION OF OIL SHALES

By

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INTRODUCTION

NMR and ESR have proven to be very useful methods for studying various properties of fossil fuels. Although most studies have been applied to coals, in recent years an increasing emphasis has been placed on using magnetic resonance to study oil shales. One of the most important recent developments involves the use of C-13 NMR. Using cross-polarization and magic-angle spinning, separate aliphatic and aromatic C-13 peaks can be resolved (1). It has been shown for oil shales that the Fischer Assay determination of oil yield is strongly correlated with the aliphatic signal (2, 3).

Proton NMR has also been useful in characterizing oil shales. Several investigators have shown that the total proton NMR signal is linearly correlated with the oil yield if oil shale samples of a similar type are compared (4-7). Temperature-dependent relaxation time measurements can also be useful. Miknis and Wetzel (5) reported  $T_1$  values of a Western shale and its kerogen concentrate which had a temperature dependence which reflected some characteristic motion of the kerogen. Harrell and Kohno (8) have shown that  $T_{1\rho}$  measurements can also be useful in identifying molecular motions. Lynch and co-workers (9) have shown that transient second moment measurements can help to identify thermal changes that occur in shales when they are heated.

Although a considerable amount of ESR work has been done on coal (10), by comparison, very little work has been reported for oil shales. Eaton and co-workers (11, 12) have used ESR to study a set of Wyoming oil shale samples which were nearly all obtained from different depths from the same bore hole. They showed that the integrated intensity of the organic free radical signal was linearly correlated with the oil yield. Harrell and co-workers (8, 13) have recently shown that the ESR spectra of Eastern U. S. oil shales are more intense and complex than those of Western oil shales.

In this paper, we present temperature-dependent  $T_1$  and  $T_{1\rho}$  results and ESR and ENDOR measurements on Eastern and Western U. S. oil shales.

EXPERIMENTAL

Samples

Most of the oil shale samples and their oil Fischer Assays were supplied by the Mineral Resources Institute of the University of Alabama. Two additional Western shale samples from Colorado were supplied by Exxon Research and Engineering Company. Untreated or raw shale samples (with associated oil Fischer Assays in gallons per ton, GPT) were from the following locations: Madison Co., Alabama (12.3 GPT), Limestone Co., Alabama (16 GPT), Dekalb Co., Alabama (~1 GPT), Franklin Co., Tennessee (9.5 GPT), Powell Co., Kentucky (16.9 GPT), Wyoming (60 GPT) and Colorado (25 and 33 GPT). The beneficiation products of Madison Co., Alabama and Wyoming samples with different kerogen concentrations were prepared by fine grinding and flotation (14) and had Fischer Assays in the ranges 0.3 GPT to 27 GPT and 5 GPT to 91 GPT, respectively. Madison Co., Alabama spent shales were also used. The Alabama and Tennessee shales were from the Chattanooga formation, the Kentucky shale was from the New Albany formation, the Wyoming shale was from the Mahogany Zone formation and the Colorado shales were from the Green River formation. The Dekalb Co., Alabama shales were deformed shale from a geologically folded region.

NMR

The pulse NMR system consisted of a 36 MHz Spin-Lock CPS-2 spectrometer controlled by an external digital pulse programmer. Free-induction-decay signals were recorded on a Nicolet

Explorer III digital oscilloscope which was interfaced to a microcomputer for signal averaging of weak signals. Temperature control was achieved by a gas-flow system with an electronic regulator.  $T_1$  measurements were made using a saturation- $\tau$ -90° pulse sequence and  $T_{1\rho}$  measurements were made using a 90° pulse followed by a 90° phase-shifted spin-locking pulse of variable length.

### ESR and ENDOR

ESR measurements were made on X-band and K-band systems which employed 17 kHz and 33.5 kHz field modulation frequencies. Spin concentration measurements were made at K-band by digitally integrating the first-harmonic signal. Signals were compared with the signal from a fixed amount of  $\text{Cr}^{3+}$  which was placed near the shale in the ESR cavity and which had a sufficiently different g-factor so that almost no signal overlap with the shale occurred. The  $\text{Cr}^{3+}$  was calibrated against a ruby standard obtained from the National Bureau of Standards. Saturation measurements of the line components were made at X-band using second-harmonic detection because of the better resolution as compared to the first-harmonic signal. G-factor measurements were made at K-band using second-harmonic detection. ENDOR measurements were made at X-band using field modulation and second-harmonic detection.

## RESULTS

### NMR

In general, the  $T_1$  and  $T_{1\rho}$  relaxation measurements were nonexponential and were characterized by a distribution of relaxation times. For simplicity effective  $T_1$  and  $T_{1\rho}$  values, defined as  $t_{1/2}/\ln 2$ , were determined. For  $T_1$ ,  $t_{1/2}$  was the time for the longitudinal magnetization to recover to within one-half of the thermal equilibrium value following a saturation sequence. For  $T_{1\rho}$ ,  $t_{1/2}$  was the duration of a spin-locking pulse in a  $T_{1\rho}$  sequence such that the transverse magnetization decayed by a factor of one-half.

$T_1$  and  $T_{1\rho}$  values for all of the raw shales were measured as a function of temperature from about -135°C to 280°C. Results for the Limestone Co., Alabama and Wyoming shales are shown in Figures 1 and 2 as representative results for the Eastern and Western shales. The  $T_1$  values for all of the samples had a temperature dependence which was similar to that shown in Figures 1 and 2, although the magnitudes varied from shale to shale. At room temperature, the  $T_1$ 's ranged from a low of 4 ms for the Kentucky shale to a high of 40 ms for the Madison Co., Alabama shale. For all samples, essentially no variation in  $T_1$  with temperature was observed below room temperature.  $T_1$  increased with increasing temperature starting in the range from about 20°C to 85°C. For some samples a shallow  $T_1$  minimum was also observed in this temperature region. When the samples were evacuated overnight,  $T_1$  was observed to either increase or to remain unchanged. The greatest change, a factor of about two, occurred for the Limestone Co., Alabama shale, as shown in Figure 1, while essentially no change occurred for the Madison Co., Alabama shale.

The  $T_{1\rho}$  values of all of the Eastern shales were nearly the same both in magnitude and in temperature dependence. Almost no change occurred in  $T_{1\rho}$  as a function of temperature except for a slight increase in  $T_{1\rho}$  at the highest temperatures for some of the samples. The Limestone Co., Alabama  $T_{1\rho}$  values shown in Figure 1 had about the same dependence upon  $H_1$  over the entire temperature range. When  $H_1$  was increased from 3 G to 16 G,  $T_{1\rho}$  increased by a factor of about two.

The  $T_{1\rho}$  results for the Western shales exhibited the most detail of all of the relaxation measurements. Both Colorado shales gave  $T_{1\rho}$  results almost identical to those shown in Figure 2 for the Wyoming shale. A broad minimum centered at -75°C and a sharp minimum centered at 182°C were detected. The dependence upon  $H_1$  in the vicinity of the low-temperature minimum was about the same as for the Eastern shales. However, a stronger  $H_1$  dependence was detected near the high-temperature minimum, with the largest dependence detected on the low-temperature side of the minimum. In contrast to the  $T_1$  case, almost no change was observed in  $T_{1\rho}$  for either Eastern or Western shales after they were evacuated.

### ESR and ENDOR Spectra

All oil shale samples exhibited ESR signals which were characteristic of organic free radicals. In addition, weak vanadium signals in the Eastern shales and manganese signals in the Western shales could be detected.

The organic free radical spectra of all of the raw Eastern oil shales were similar to the Madison Co., Alabama spectrum shown in Figure 3. Three well-defined components can be easily detected in this X-band spectrum. At K-band these components were more clearly resolved. G-factors measured at K-band were 2.0028, 2.0018 and 2.0006, from left to right. The sample used to obtain the spectrum of Figure 3 consisted of finely ground particles which had been exposed to air for about 30 minutes before the spectrum was obtained. When the sample was evacuated overnight and the spectrum remeasured, an additional sharp component appeared in the spectrum as shown in

Figure 4. This peak overlaps the broad low-field component but appears to have a slightly smaller g-factor. This peak was even more intense in the spectrum of a fresh sample which was crushed to millimeter-size pieces and quickly measured in air.

The saturation behavior of a Madison Co., Alabama oil shale spectrum taken in air is shown in Figure 5. As indicated in the figure, the amplitude of the spectrum at four different positions is plotted as a function of relative microwave power. Because of the overlap of the spectral components, this curve does not accurately represent the saturation behavior of the individual components. However, it is quite clear that the high-field peak is easily saturated relative to the other peaks.

All of the raw Eastern oil shale samples had line components with g-factors and widths which were approximately the same as those for the Madison Co., Alabama shale, although the relative amplitudes of the components varied. Beneficiated Madison Co., Alabama samples exhibited spectra which had less resolution than those which were obtained from the raw, untreated Eastern shales. Spent Madison Co., Alabama shales showed a single broad in-phase component and no out-of-phase component, implying a very short  $T_1$ . The Western shale spectra consisted primarily of a single broad component. In addition, some Western spectra exhibited a weak, sharp component which had a g-factor approximately the same as that of the high-field component in the Eastern shales.

ENDOR spectra were measured from a Madison Co., Alabama shale sample in order to obtain information about the nuclear environment of the free radicals. Both in-phase and out-of-phase ENDOR signals were measured from different parts of the ESR spectrum. Figure 6 shows in-phase and out-of-phase spectra obtained from the low-field part of the ESR signal. Although the signal is displayed in the figure as positive, it is actually negative. Only a broad matrix ENDOR signal centered at the free-proton frequency of 13.8 MHz was obtained. Similar signals were obtained from other parts of the ESR spectrum. Because of the overlap of the individual ESR line components and because of the weak signal-to-noise ratio, no significant differences in the hyperfine interactions of the different components could be determined.

#### Spin Concentrations

Spin concentrations were determined for raw, untreated shales, for beneficiated Madison Co., Alabama and Wyoming shales, and for spent beneficiated Madison Co., Alabama shales. When comparing raw shales, the spin concentration generally decreased as the Fischer Assay increased. The deformed Dekalb Co., Alabama shales, which had a Fischer Assay of about 1 GPT, had the largest spin concentration and the Wyoming shale, with a Fischer Assay of 60 GPT, had the smallest spin concentration.

Figure 7 is a plot of spin concentration as a function of the amplitude of the hydrogen free-induction-decay signal per unit mass of sample. This plot shows that when comparing beneficiated shales of a given type, that is, either the Madison Co., Alabama or the Wyoming shales, a linear relationship is seen to exist between the spin concentration and the hydrogen NMR signal. The graph shows that this linear relationship is preserved when the Madison Co., Alabama shales are pyrolyzed in the Fischer Assay process to yield spent shales. The spin concentration also appears to be linearly related to the hydrogen NMR signal for the raw Dekalb Co., Alabama deformed shales. The straight lines do not extrapolate through the origin.

## DISCUSSION

### NMR

There is strong evidence to suggest that interactions between protons and paramagnetic centers may be a significant  $T_1$  relaxation mechanism in the oil shales. The  $T_1$  values are much lower than one would expect due to other likely relaxation mechanisms. The weak temperature dependence below room temperature is typical of relaxation due to paramagnetic centers (15). The removal of paramagnetic oxygen by evacuation increases  $T_1$ . Also, ESR shows that paramagnetic centers do exist in the shales. If paramagnetic centers do contribute significantly to the relaxation, then one might expect to observe a correlation between  $1/T_1$  and the spin concentration; however, no such correlation was observed. However, in view of the complex and heterogeneous composition of the shales, this lack of correlation does not rule out this possible relaxation mechanism. It might be more reasonable, for example, to expect a correlation between  $1/T_1$  and the number of spins per unit mass of total organic matter or per unit mass of aromatic material, rather than total sample mass. The high-temperature  $T_1$  behavior suggests that there is some characteristic motion occurring in this range which is common to all the shales. This observation is in agreement with the work of Mknis and Wetzel (5).

It is difficult to determine what relaxation mechanisms are responsible for the  $T_{1\rho}$  results, especially for the Eastern shales. The lack of variation in  $T_{1\rho}$  for the Eastern shales from sample to sample and the observation that  $T_{1\rho}$  does not change when the samples are evacuated

suggest that relaxation due to paramagnetic centers may not be very important. Since there is essentially no variation in  $T_{1\rho}$  with temperature for the Eastern shales, no motional information can be obtained from the data. The reason for this lack of variation may be in part because the Eastern shales have a highly aromatic and somewhat rigid molecular structure.

In contrast with the Eastern shales, the  $T_{1\rho}$  results for the Western shales provide clear evidence of molecular motion. The low-temperature  $T_{1\rho}$  minimum is probably caused by the same type of motions that give rise to the high-temperature variation in  $T_1$ . The high-temperature  $T_{1\rho}$  minimum depicts a motion which cannot be observed in the  $T_1$  data. Lynch et al. (9) have reported a second moment reduction in a highly aliphatic Australian shale at a temperature similar to that for the high-temperature  $T_{1\rho}$  minimum. They liken the motion producing this reduction to a glass to rubber-type transition in an amorphous polymer. The high-temperature  $T_{1\rho}$  measurements may be evidence of a similar type of motion.

Some insight in understanding the relaxation mechanisms involved in the oil shales might be obtained by making comparisons with simpler model systems such as polymers. For example, there are similarities between the results presented here and those found for poly(vinylidene fluoride) (PVF<sub>2</sub>) in which slow spin diffusion was found to be important in explaining the  $T_{1\rho}$  results (16).

### ESR and ENDOR

The unusual nature of the ESR spectra of the Eastern shales is of particular interest. The two overlapping low-field components, including the oxygen effect, are similar to results which have been reported for bituminous coals (17, 18). However, the high-field peak is unusual in its combination of narrow line width, the ease with which it saturates and its low  $g$ -factor. To our knowledge, these spectra are unlike any other spectra which have been previously reported for fossil fuels.

Although the ENDOR results are unable to reveal differences between the nature of the different components of the Eastern ESR signals, the existence of a matrix ENDOR signal is evidence that some of the free radicals have a hydrogen environment. The difficulty of detecting separate ENDOR signals due to overlapping ESR line components might be partially resolved if ENDOR measurements were made at K-band where the line components are more widely separated. The ENDOR spectra in Figure 6 are similar to the negative ENDOR spectra obtained by Miyagawa et al. (17) for various components of bituminous coal from Alabama. However, we know of no other reported ENDOR spectra which have been obtained from oil shale.

The linear relationship that we have observed between the spin concentration and the hydrogen density as determined by the NMR signal for beneficiated samples suggests that the ESR signal is primarily of organic origin. The extrapolation of these straight lines to zero spin concentration suggests that there is an appreciable amount of hydrogen-bearing material in the shales which contain no free radicals.

The decrease in spin concentration with increasing oil yield that we have observed for the raw shales appears to differ from the linear relationship that Eaton and co-workers have observed (11). However, this apparent inconsistency may be resolved if one considers the free radicals to be based primarily in the aromatic fraction of the oil shale and the oil yield to depend primarily upon the aliphatic fraction.

### CONCLUSIONS

It has been shown that relaxation measurements can be useful in characterizing motions in oil shales. High-temperature  $T_{1\rho}$  measurements have been shown to be especially useful in showing molecular motions that may be related to the oil producing aliphatic part of the shale. However, in order to more fully exploit relaxation measurements, a more fundamental understanding of the relaxation mechanisms must be obtained.

Because the ESR spectra of the Eastern oil shales have been found to be so rich in detail, it may be possible to learn more about the nature of the free radicals in shales than is now known for coal, which has been studied much more extensively. Clearly, additional work on this subject should prove fruitful.

In order to more fully evaluate the utility of using spin concentrations as a measure of the resource potential of oil shales, measurements must be made on a larger number and a greater variety of shales.

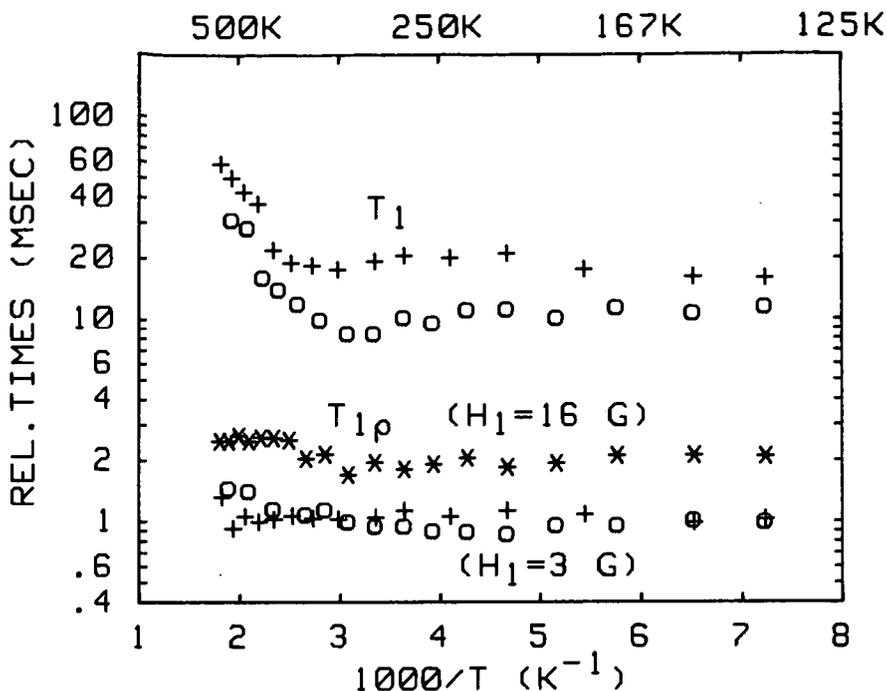


Figure 1.  $T_1$  and  $T_{1\rho}$  results for shale from Limestone Co., Alabama. Points indicated by (+) are for evacuated sample. Other points are for sample exposed to air.

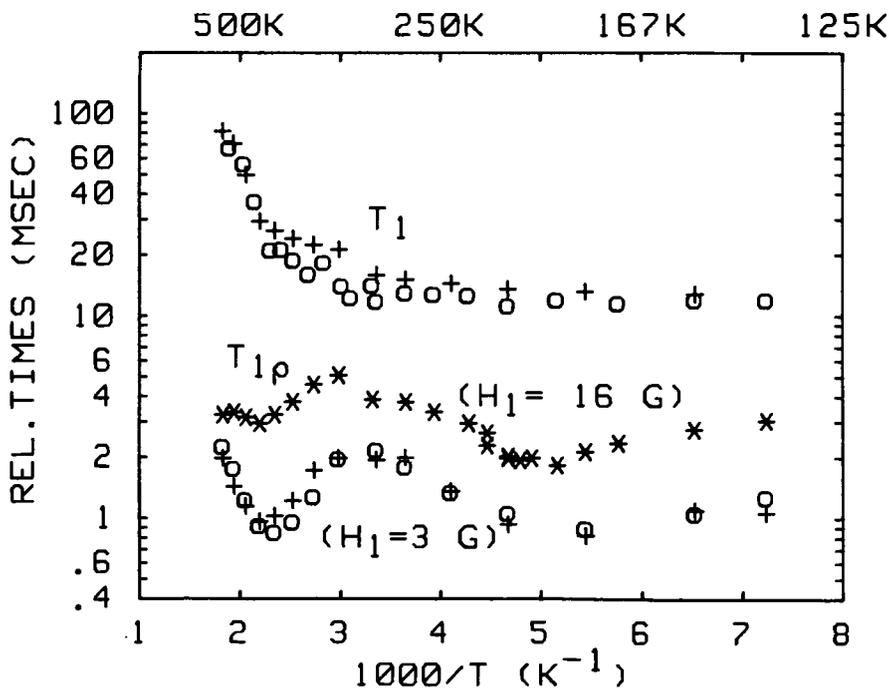


Figure 2.  $T_1$  and  $T_{1\rho}$  results for shale from Wyoming. Points indicated by (+) are for evacuated sample. Other points are for sample exposed to air.

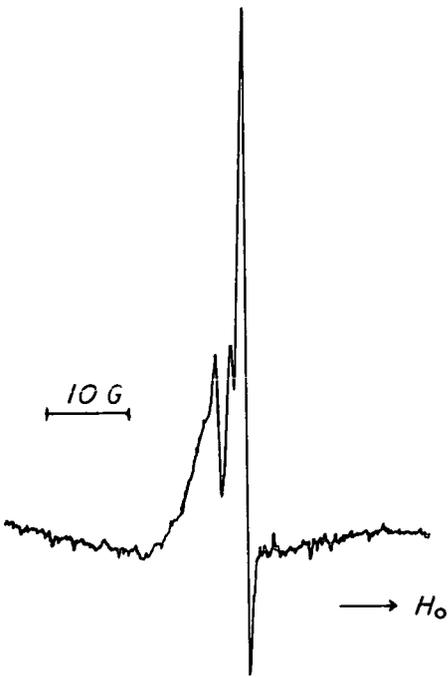


Figure 3. ESR spectrum of shale from Madison Co., Alabama exposed to air and taken at X-band using 2nd harmonic detection.

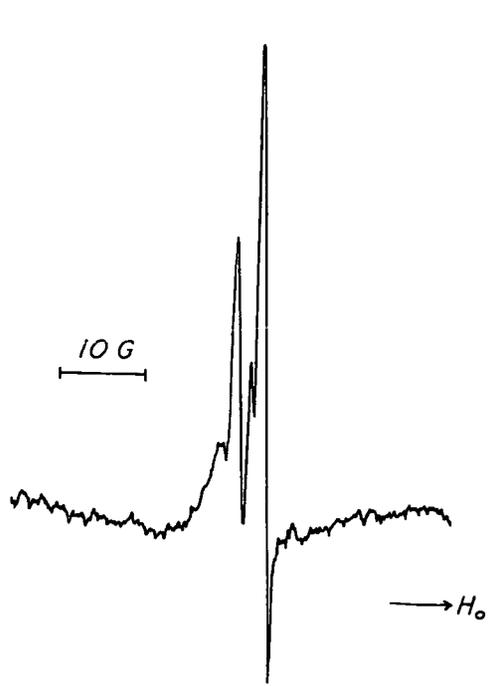


Figure 4. ESR spectrum of evacuated shale sample from Madison Co., Alabama.

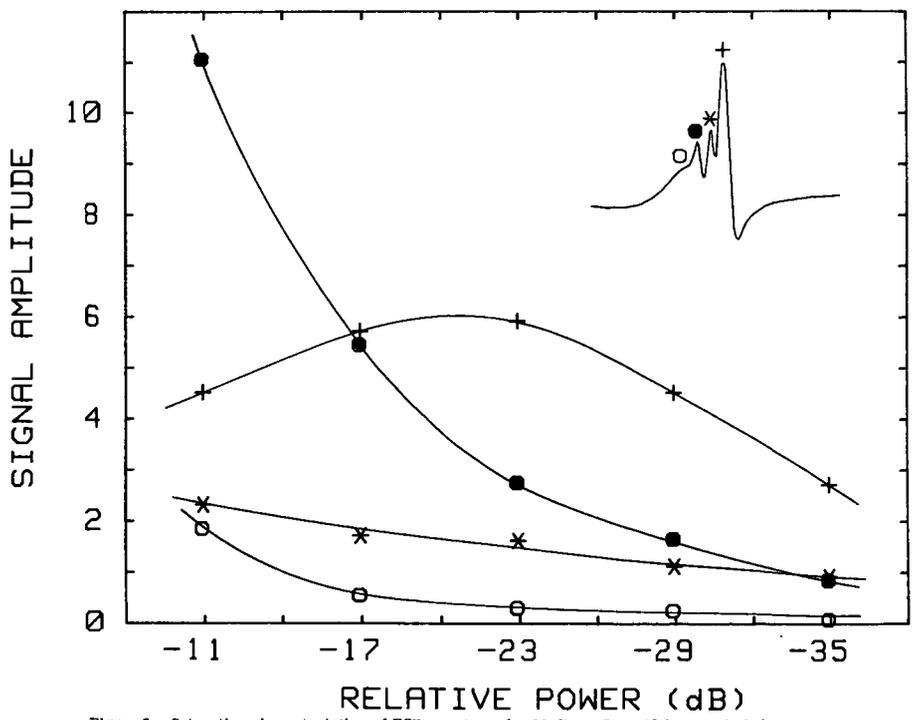


Figure 5. Saturation characteristics of ESR spectrum for Madison Co., Alabama oil shale.

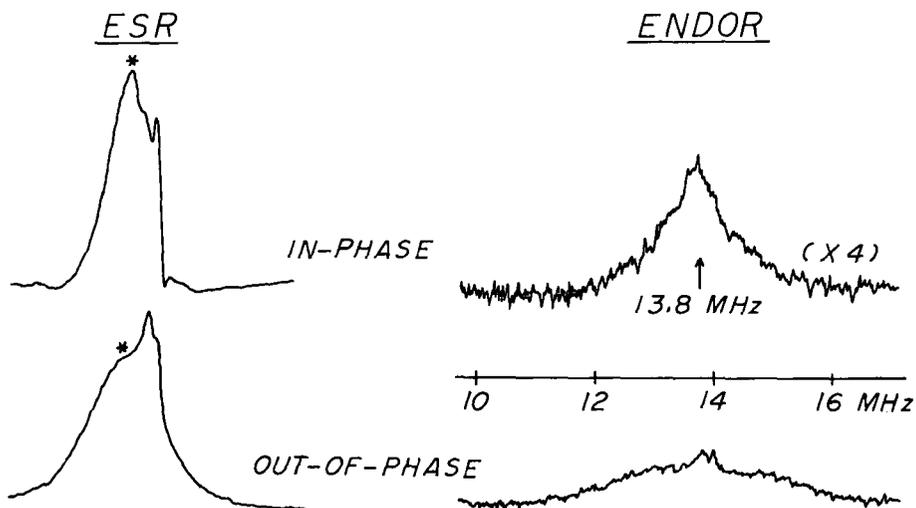


Figure 6. ENDOR spectra taken from low-field part of ESR signal.

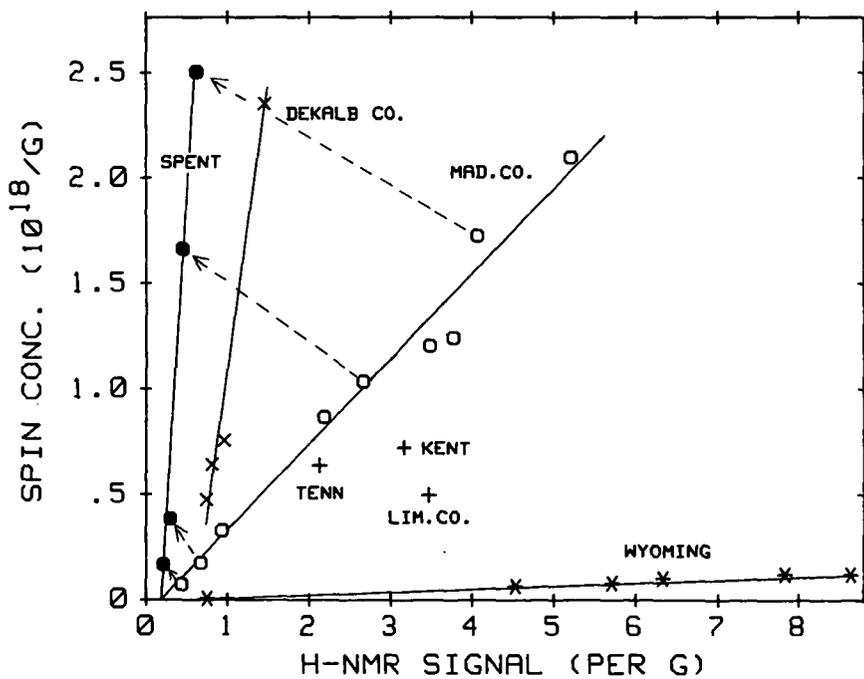


Figure 7. Spin concentration versus amplitude of proton free-induction-decay signal.

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